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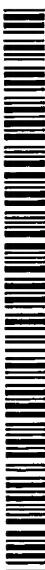
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**WO 01/85606 A1**

(54) Title: **METHOD OF HYDROGEN GENERATION FOR FUEL CELL APPLICATIONS AND A HYDROGEN-GENERATING SYSTEM**

(57) Abstract: **Hydrogen is generated by reaction of a metal hydride and at least one alcohol which may be employed in conjunction with water; this provides a convenient, efficient method of generating hydrogen for a fuel cell.**

## METHOD OF HYDROGEN GENERATION FOR FUEL CELL APPLICATIONS AND A HYDROGEN-GENERATING SYSTEM

### 5 TECHNICAL FIELD

The invention discloses a method of generating hydrogen for fuel cell applications, based on a chemical reaction of metal hydrides with alcohols, the invention also relates to a hydrogen generator using such reaction is described.

### 10 BACKGROUND ART

Fuel cells require a continuous supply of hydrogen and oxygen to produce electricity. At present however, storage and supply of hydrogen is the main 15 limiting step in the use of fuel cell systems. For vehicular applications, large amounts of hydrogen, typically of the order of several kilograms, are needed on-board between refuelling. However, current methods of hydrogen storage not only cannot provide sufficient hydrogen capacity, or volumetric density, to compete with gasoline cars, but have additional serious limitations. For example, 20 compressed hydrogen tanks operate at very high hydrogen pressure, typically 350 – 700 atm and so have a serious safety problem. Liquid hydrogen on the other hand needs cryogenic temperatures, typically about ten to fifteen degrees above absolute zero, and therefore requires costly and demanding cryogenic equipment. In the case of miniature fuel cells for portable applications, for 25 example for laptops or cellular phones, the hydrogen storage is even more critical, because both of these storage methods are totally impractical on the small scale.

Metal hydrides offer a good solution for hydrogen storage: they are safe, stable and provide indefinite storage without hydrogen loss. In general, the use of 30 metal hydrides is based on the reversible cycling of hydrogen absorption and desorption under certain pressure/temperature conditions. A variety of metal hydrides is known, having various hydrogen capacities and different pressure/temperature characteristics.

In general, metal hydrides can be divided into two groups:

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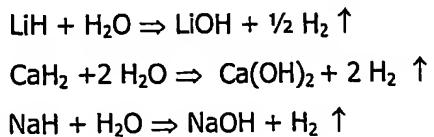
- a) "unstable" hydrides operating at room temperature. These hydrides require hydrogen pressure, typically between 2 and 5 atm, to be maintained in the tank, otherwise the hydrogen is immediately released from the hydride. These room-temperature hydrides, for example those based on LaNi<sub>5</sub> or FeTi,  
5 provide easy and fast hydrogen desorption, but have low hydrogen storage by weight, typically around 1 wt.%.
- b) "stable" hydrides operating at elevated temperatures. These metal hydrides can indefinitely store hydrogen at room temperature, even without  
10 hydrogen overpressure. However, desorption requires raising the temperature, in some cases significantly. For example, Mg-based hydrides need to be heated to temperatures close to 300°C in order to release hydrogen. Although these hydrides have high hydrogen capacities, reaching 7.6 wt.% in the case of MgH<sub>2</sub>, the high temperature of hydrogen desorption is a serious practical disadvantage.  
15
- Very few metal hydrides are known where thermodynamic properties allow reversible operation at moderate temperature, such as temperatures below or around 100°C, and also having good hydrogen capacity. One example is NaAlH<sub>4</sub>, which can operate reversibly with good kinetics and hydrogen capacity of 5.6  
20 wt.%, but only after advanced catalysis [1,2]. However, currently even catalyzed NaAlH<sub>4</sub> becomes impractically slow at temperatures below 100°C, which is required for the PEM fuel cell applications.
- An alternative method for generating hydrogen from these stable hydrides  
25 without the need to raise the temperature is through a chemical reaction leading to the decomposition of the hydride. For example, water may be used to release hydrogen via hydrolysis reaction. Water reacts with certain metal hydrides, forming hydroxides and the release of gaseous hydrogen.
- Hydrolysis has been used in a series of hydrogen generators. For example, U.S.  
30 Pat. 4,155,712 [3] discloses a small generator containing metal hydride which produces hydrogen in the reaction with water vapor. Another U.S. Pat. 4,356,163

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[4] discloses utilizing a chemical reaction of an alkali metal with water for the hydrogen generation.

Examples of the hydrolysis reaction are as follows:

5



10 Generation of hydrogen by a hydrolysis reaction is effective, but has disadvantages. One is that hydrolysis reactions are usually violent and generate large amounts of heat. Once started, they are extremely difficult to control and may proceed in an explosive manner. For example, in the case of LiAlH<sub>4</sub>, the heat of hydrolysis causes a very rapid increase of temperature, which results in an instant thermal decomposition of the hydride, so that the reaction cannot be controlled by simply limiting the amount of water, and proceeds rapidly once initiated. One way around this is to immerse the hydride in a mineral oil [5], which makes the reaction more controllable. This however reduces the effective hydrogen capacity at least by half, because the oil-based slurry needs to contain  
15 about 50 wt.% of the mineral oil. Another method to avoid explosive reaction is disclosed in U.S. Patent 5,593,640 [6], where a combination of adiabatic hydrolysis and thermal decomposition is claimed to provide a controllable generation of hydrogen. In this generator, LiAlH<sub>4</sub> is allowed to undergo hydrolysis only at temperatures exceeding the temperature of the initiation of  
20 thermal decomposition, which is effected by heating the hydride before hydrolysis in a complex generator.

The use of sodium hydride instead of lithium hydrides results in a less violent reaction, but at the expense of hydrogen capacity, which is reduced simply because sodium is much heavier than lithium. A hydrogen generator based on  
25 the hydrolysis of sodium hydride is disclosed in U.S. Patents 5,728,464 and 5,817,157 [7,8]. This reaction has however another disadvantage. It requires a significant excess of water, because the reaction product, sodium hydroxide,

causes solidification of the solution when its content exceeds 50 mol%, thus stalling any further hydrolysis.

Among other hydrides,  $\text{NaBH}_4$  reacts with water only when specially catalysed, for example by a special Ru-based catalyst [9]. In this case however, the same 5 problems as with  $\text{NaH}$  occur, namely precipitation of the solid reaction product,  $\text{NaBO}_2$ , which requires the  $\text{NaBH}_4$  solution to be diluted to 20 mol% of  $\text{NaBH}_4$  and thus results in reduced hydrogen capacity. Another technical problem is that controlling the reaction can be done only by either immersing the catalyst in the solution, which promotes the reaction or by completely removing the catalyst 10 from the solution, which stops the reaction, so that intermediate reaction rates are not accessible. In another design of the hydrogen generator it was pointed out that for portable applications the heat of hydrolysis of  $\text{NaBH}_4$ ,  $\text{LiBH}_4$ ,  $\text{LiAlH}_4$  or  $\text{NaAlH}_3$  is so large that the hydrolysis-based generators could be too hot to be practical. In these cases the heat of hydrolysis is used to generate steam for the 15 steam-hydrolysis of the hydrides [10].

All hydrolysis reactions have also one common problem: the use of water limits the temperature range of the hydrogen generator to temperatures above 0°C, to avoid freezing of the water. This is a serious limitation for the outdoor use of 20 the hydrolysis-based generators in a cold climate, which may require a "cold start-up" at temperatures below -20°C, or even -40°C.

Thus at present, none of the above methods of storing and generating 25 hydrogen represents a fully efficient, safe and reliable source of hydrogen for fuel cells. All the above methods suffer from serious limitations and therefore alternative methods of hydrogen generation are needed. It is the aim of the present invention to offer such an alternative method.

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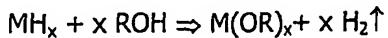
### **DISCLOSURE OF THE INVENTION**

5 In accordance with one aspect of the invention there is provided a process for generating hydrogen from a metal hydride comprising: reacting a metal hydride with at least one alcohol.

10 In accordance with another aspect of the invention there is provided a hydrogen generator comprising: a) a first housing containing a metal hydride; b) a second housing containing at least one alcohol for reaction with said metal hydride, c) flow means for delivery of said at least one alcohol from said second housing to said first housing, and d) hydrogen gas outlet means in said first housing for delivery of generated hydrogen gas from said first housing.

### **DETAILED DESCRIPTION OF THE INVENTION AND DESCRIPTION OF PREFERRED EMBODIMENTS**

15 The present invention relates to a new method of hydrogen generation particularly for fuel cell applications. In this method, hydrogen is produced from a metal hydride in a chemical reaction with an alcohol. The metal hydride may 20 be a simple metal hydride or a complex metal hydride. In the case of a simple metal hydride the reaction proceeds by the following generic reaction which is the basis for the hydrogen production:



25 in which  $\text{MH}_x$  is a simple metal hydride and ROH is an alcohol. In the above metal hydride M is, by way of example, typically Li, Na, K, Mg, Ca, Be, Sr, K, Nb, Zr or Ti; R is typically an alkyl group of 1 to 10, preferably 1 to 6 and more preferably 1 to 4 carbon atoms, for example, methyl, ethyl, n-propyl, iso-propyl, 30 n-butyl, sec.butyl or tert.butyl. The designation x is an integer typically of 1 to 4.

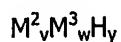
In this reaction, the metal atom (M) from the hydride substitutes hydrogen in the hydroxyl group (OH) in the alcohol. As a result, another compound is formed,

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namely, an alkoxide, and hydrogen is released from the metal hydride and, from the alcohol.

The above exemplification of the process is made for ease of description for the case of a simple metal hydride; however, the hydrogen generation proceeds  
5 similarly with complex metal hydrides and with mixtures of simple and complex metal hydrides.

By way of example, complex metal hydrides which may be employed in the invention include those of formula:



10 in which  $M^2$  is metal selected from the group consisting of Li, Na, K, Mg, Ca, Fe and Zr;  $M^3$  is selected from the group consisting of Al, B, Be and Ti; v is an integer of 1 to 3; w is an integer of 1 to 3; and y is an integer of 4 to 8.

However, the invention extends to all metal hydrides and is not confined to the particular subclasses of metal hydride or specific metal hydrides referred to in  
15 the illustration of the invention herein.

By way of example metal hydrides for use in the invention include simple alkali metal hydrides such as LiH, NaH, KH, RbH, CsH, hydrides of the elements of main group II metal BeH<sub>2</sub>, MgH<sub>2</sub>, CaH<sub>2</sub>, SrH<sub>2</sub>, BaH<sub>2</sub>, metallic-type hydrides e.g. ScH<sub>2</sub>, YH<sub>2</sub>, YH<sub>3</sub>, TiH<sub>2</sub>, ZrH<sub>2</sub>, HfH<sub>2</sub>, VH, VH<sub>2</sub>, NbH, NbH<sub>2</sub>, TaH, PdH,  
20 rare earth hydrides e.g. LaH<sub>2</sub>, CeH<sub>2</sub>, PrH<sub>2</sub>, NdH<sub>2</sub>, SmH<sub>2</sub>, GdH<sub>2</sub>, DyH<sub>2</sub>, TbH<sub>2</sub> covalent hydrides e.g. CuH, ZnH<sub>2</sub>, AlH<sub>3</sub>, GaH<sub>3</sub>, InH<sub>3</sub>, ThH<sub>3</sub>, SnH<sub>4</sub>, PbH<sub>4</sub> and boranes, silanes and germanes, + mixed (complex) hydrides of the above elements, e.g. ternary etc, for example LiAlH<sub>4</sub>, (Li-Na)AlH<sub>4</sub>, LiBH<sub>4</sub>, NaBH<sub>4</sub>, KBH<sub>4</sub>, and their non-stoichiometric hydrides and solid solutions.

25 Metal hydrides have been found to readily react with alcohols, for example with methanol, ethanol or higher alcohols, and the reaction produces a steady and abundant flow of hydrogen at room temperature and below.

Thus the invention has the advantage that the process proceeds conveniently at temperature below 30°C, preferably below 25°C and 20°C and below. Moreover,  
30 the amount of the hydrogen released is greater than that obtained from the thermal decomposition of the hydride, because hydrogen comes not only from the hydride, but also from the hydroxyl group of the alcohol.

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Table I summarizes nominal hydrogen capacities obtained from various metal hydrides in the alcoholysis reaction of the invention. The hydrogen capacities are given in wt % with respect to the weight of the hydride, and also in hydrogen volume obtained in the alcoholysis reaction from 1 kilogram of the hydride. Total  
5 hydrogen capacities, including both the weight of the hydride and weight of alcohol are also listed. Although in some reactions an excess of alcohol is advantageous for the reaction rate, the alcohol excess was not taken into account in the Table. It should be noted here that in the case of more complex reactions, for example involving bi-metallic hydrides (i.e. with two different metal atoms) the overall hydrogen capacities are dependent on the reaction route and  
10 may change depending on the applied temperature, catalysis and excess of the alcohol.

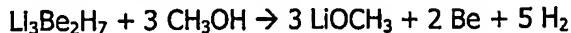
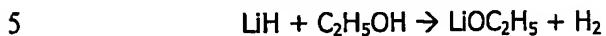
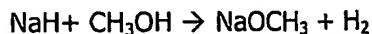
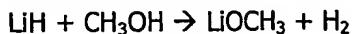
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TABLE I

Hydride	wt. % of H <sub>2</sub> (in respect to the hydride weight)	Litres of H <sub>2</sub> obtained per 1 kg of hydride	Total H <sub>2</sub> capacity (including the weight of the hydride and the alcohol - methanol)
LiH	25.4	2845	5.0
LiAlH <sub>4</sub>	13.2	1478	7.2
Li <sub>3</sub> AlH <sub>6</sub>	16.8	1882	6.1
LiBH <sub>4</sub>	23.1	2592	9.4
NaH	8.3	933	3.6
NaAlH <sub>4</sub>	9.3	1045	5.9
Na <sub>3</sub> AlH <sub>6</sub>	8.9	996	4.6
NaBH <sub>4</sub>	13.3	1490	7.3
Li <sub>3</sub> Be <sub>2</sub> H <sub>7</sub>	22.0	2460	7.1
Li <sub>2</sub> BeH <sub>4</sub>	22.5	2516	6.7
MgH <sub>2</sub>	15.3	1716	4.5
CaH <sub>2</sub>	9.6	1074	3.8
FeTiH <sub>2</sub>	5.7	641	2.6
ZrH <sub>2</sub>	4.3	484	2.6
TiH <sub>2</sub>	8.1	905	3.5
MgAl <sub>2</sub> H <sub>8</sub>	11.7	1307	6.7
LiAl <sub>2</sub> H <sub>7</sub>	11.9	1329	8.1
ZrAl <sub>2</sub> H <sub>8</sub>	6.6	737	4.6

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Examples of the specific reactions of hydrogen generation are as follows:



According to these reactions, metal hydrides produce alkoxides and hydrogen in  
10 the reaction with alcohols. Metal alkoxides are derivatives of alcohols (MOR) and  
constitute an important branch of organometallic chemistry. The research on  
alkoxides was initiated more than a century ago and now alkoxides find a variety  
of important applications, for example as drying agents, water-repellents, and  
paint components. The most common catalytic applications of alkoxides include  
15 redox catalysis and olefin polymerization catalysis. Alkoxides are also used as  
precursors to metal oxides. High purity oxides can be obtained through  
hydrolysis, pyrolysis or combustion of alkoxides. Metal alkoxides are usually  
produced by one of the following methods (as widely described for example in a  
review book "Metal alkoxides" [11]):

- 20
  - reaction of metals with alcohols
  - reaction of metal halides with alcohols
  - reaction of metal hydroxides and oxides with alcohols
  - alcohol interchange
  - transesterification reactions
- 25
  - reactions of metal dialkylamides with alcohols.

Although alkoxides can be effectively produced by all these techniques and most  
of the above methods are used on an industrial scale, the formation of alkoxides  
from hydrides has been never considered in practice probably for a number of  
30 reasons. First, the hydrides now found to be very efficient in the generation of  
hydrogen in the alcoholysis reactions, were previously either very difficult to  
fabricate, as for example Mg hydride, or Na<sub>3</sub>AlH<sub>6</sub>, or not known, for example Li-

- 10 -

Be hydrides, or (Li-Na)-Al hydrides. Only recent advances in metal hydrides synthesis by solid-state reactions enabled easy fabrication of many hydrides [13]. Another reason not to consider formation of alkoxides from hydrides, especially when the use of metals is sufficiently effective, is that the release of 5 hydrogen from the hydride could be a serious complication during the alkoxide production. This potentially negative feature of the alcoholysis reaction is the key of the hydrogen generation in the present invention.

As seen in Table 1, various hydrides can be used for the hydrogen production, 10 and the optimum hydride can be chosen based on the required hydrogen capacity, the hydride cost and the required reaction rate.

Methanol, CH<sub>3</sub>OH is the simplest and the lightest of all alcohols, therefore alcoholysis of metal hydrides with methanol gives the highest total hydrogen capacity, as shown in the Table. However, ethanol or higher alcohols provide 15 much better reactivity with certain hydrides, for example complex borohydrides or calcium hydride CaH<sub>2</sub>. The type of alcohol in the hydrogen generator can be chosen depending on the metal hydride, and also on the required reaction route and kinetics. Since alcohols are easily mixable, a mixture of two or more alcohols can be used in a very wide proportion. For example, a mixture of methanol and 20 ethanol can be used, where methanol provides higher overall hydrogen capacity and ethanol better reactivity. The appropriate proportion of methanol/ethanol mixture can be adjusted during the efficiency testing of the hydrogen generation.

25 As mentioned above, the crucial advantage of the alcoholysis reaction over the hydrolysis reaction, is the potential of operating at temperatures below the freezing temperature of water. Even more convenient however is to use a mixture of alcohol and water, a common "windshield fluid", to produce hydrogen. In this case, the reaction is a combination of alcoholysis and 30 hydrolysis, with two great enhancements over the hydrolysis alone: a more controllable reaction rate and possible operation at temperatures much below 0°C. The main advantage of the hydrogen generator based on the combined

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hydrolysis and alcoholysis is its flexibility to the "reactive liquid" used. The "reactive liquid", i.e. the mixture of alcohol, or alcohols, with water can be adjusted depending on the climate or season, with a higher proportion of alcohol in the liquid when operating at lower temperatures is required, and with more  
5 water when more rapid hydrogen desorption is needed.

In certain cases, as for example in the case of alkali metal borohydrides, for example,  $\text{LiBH}_4$  and  $\text{NaBH}_4$ , the alcoholysis reaction needs to be catalyzed in order to increase the reaction rate. The addition of a solid-state catalyst can be very efficient in enhancing the reaction kinetics. Various catalysts can be used  
10 for this purpose, depending on the metal hydride and on the alcohol, for example iodine and its compounds, chlorides, or various metals, e.g. Ru, Ni, Ti and Fe and their compounds. The catalyst can be introduced either in the solid state, admixed to the hydride, or in a solution with alcohol, or dissolved in another, neutral solvent.

- 15 A single type of hydride can be used in the hydrogen generator, but in some cases a mixture of two or more hydrides can be more advantageous. The main reason for using a mixture of hydrides is modification of the reaction rate or catalysis. Usually there is no inter-reaction in the mixture of two hydrides in the  
20 powdered form at room temperature. However, when the mixture is immersed in alcohol, the reaction route, and the reaction rate, can be completely changed, as compared to the two hydrides alone. This can be effected by either formation of hetero-alkoxides, or by a combined, synergetic reaction, where the more reactive component induces the reaction of the "slower" component. This can be  
25 particularly advantageous when the slow hydride is inexpensive and has high hydrogen capacity, and the fast hydride is more expensive or difficult to fabricate. The fast reaction can induce and promote the second reaction in a synergetic way, as shown for example for hydrogen desorption in a mixture of  $\text{MgH}_2$  and  $\text{Mg}_2\text{NiH}_4$  [13].
- 30 Usually the most convenient form for the hydride, or hydrides, inside the generator before adding alcohol, or its mixture with water, is in the solid state, typically in a powdered form. However, when a fast refilling of the hydride

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container is required, the hydride may be contained in a neutral solvent, for example tetrahydrofuran or toluene, and so easily pumped into the tank.

The alcohol may be in liquid, gaseous or vapor state.

5

As described above, the alcoholysis reaction of metal hydrides leads to the formation of metal alkoxides. There are two ways of dealing with the reaction products, i.e. recovering the metals. In some cases, simple hydrolysis or pyrolysis of the alkoxides gives a very valuable oxide product of very high purity  
10 and dispersion, which is ideal for many catalytic applications. An example is magnesium oxide, zirconium oxide or titanium oxide. Alkali metals in contrast, form hydroxides, for example LiOH or NaOH, as a result of hydrolysis of the respective alkoxides, which can be subsequently thermally decomposed into lithium and sodium hydrides and returned into the hydrogen generator.

15

In a typical reduction to practice, the metal hydride, or a mixture of two or more hydrides, is allowed to react with alcohol simply by pouring or injecting the alcohol into the hydride container. As a result of the alcoholysis reaction, hydrogen gas is released. Hydrogen is directed toward a fuel cell system.  
20 Controlling the supply of alcohol, or a mixture of alcohol and water, can easily control the rate of reaction and the release of hydrogen. Gradual feeding with the "reactive liquid" regulates the amount of the produced hydrogen, and the reaction can be thus stopped or increased depending on the demand for hydrogen. In a practical way it is effected through an injection system, which  
25 reduces the supply of the "reactive liquid" in response to the increasing pressure of the produced hydrogen.

The invention also relates to a hydrogen generator as described hereinbefore. A typical hydrogen generator may have the following features or components:

1. A container with metal hydride, preferably being in a powder form, or in a solution in a neutral liquid. The container can consist of a single reaction chamber, but for large-scale application several separate  
5 reaction chambers can be more advantageous in order to have better control of the reaction.
2. A container with the "reactive liquid", e.g. the alcohol, a mixture of alcohols or a mixture of alcohol with water.
3. An injection system with a regulator for the controlled supply of the  
10 "reactive liquid" to the metal hydride.
4. A hydrogen outlet towards the fuel cell system, with pressure controller and safety gauge.

15 The above hydrogen generator can be used either as a main source of hydrogen for fuel cells, or as a start-up device only. In the latter case, the main hydrogen supply can be provided for example by thermal decomposition of metal hydrides.

#### **BRIEF DESCRIPTION OF DRAWINGS**

Fig. 1 is a schematic representation of a hydrogen generator of the invention.

20

#### **DETAILED DESCRIPTION OF DRAWINGS**

With further reference to Fig. 1, a hydrogen generator 10 comprises a container 12 for metal hydride, a container 14 for a reservoir of an alcohol, a hydrogen collection tank 16 and a hydrogen outlet conduit 18.

25

Container 12 as illustrated is modular having a plurality of discrete and separate compartments 20 for metal hydride. A feed conduit 22 connects the container 14 with a selected compartment 20.

30 Included in feed conduit 22 is a heater/cooler 24, as an optional component, a feed injector 26 and a valve 28 which controls the feed of the alcohol to the selected compartment 20.

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A conduit 30 having a valve 32 communicates container 12 with tank 16; a valve 34 is disposed in hydrogen outlet conduit 18.

- 5 In operation an alcohol or a mixture of alcohols or an aqueous alcohol or alcohol mixture is injected from container 14 to a selected compartment 20, optionally with heating or cooling in heater/cooler 24. The alcohol or other reactive alcohol mixture, with the metal hydride in the selected compartment 20 of container 12 with generation of hydrogen gas which flows from container 12 to tank 16.
- 10 Hydrogen is delivered from tank 16 via conduit 18 as required, for example, to a hydrogen fuel cell.

When the selected compartment is depleted in the metal hydride the modular compartment 20 may be replaced by a new compartment having a fresh supply 15 of metal hydride. The metal alkoxide by-product may be recovered from the exchanged modular compartment.

Although the above reactions of alcohols with metal hydrides are aimed mainly towards the generation of hydrogen, they may actually also open the door to 20 better ways for the formation of various metal alkoxides. In certain cases, complex alkoxides cannot be produced by a simple alcoholysis of metals or other compounds and the reaction with the respective hydride is the only way to produce these new alkoxides. An outstanding example is a newly synthesized Li<sub>3</sub>Be<sub>2</sub>H<sub>7</sub> hydride. In the dehydrogenated form the material simply consists of a 25 mixture of two immiscible metals: Li and Be. In the hydrogenated state however, hydrogen atoms bond Li and Be together, forming a hydride. Therefore, the alcoholysis reaction with the Li<sub>3</sub>Be<sub>2</sub>H<sub>7</sub> is different (under certain experimental conditions) than that with Li and Be alone, and therefore more complex compounds can be formed: bi-metallic alkoxides i.e. containing two different 30 metal atoms. This reaction was only possible after an efficient method of the hydride formation was developed, as described in reference [14]. Other "double" hydrides (for example LaNi<sub>5</sub>H<sub>6</sub>, FeTiH<sub>2</sub> or Mg<sub>2</sub>NiH<sub>4</sub>) also offer the possibility of

- 15 -

producing unique, double alkoxides, for which this reaction path was never considered before.

In a particular embodiment the method employs a combination of an alcohol and  
5 water, this combination gives the following advantages:

- maximization of the hydrogen production (because both reactions fully contribute to the hydrogen generation)
- fully controllable reaction rate (and route) through the adjustable  
10 contribution of the two reactions in the process (by the alcohol-to-water ratio)

For example, the normally "explosive" hydrolysis of LiAlH<sub>4</sub> can be tamed and controlled by the addition of alcohol, without sacrificing the hydrogen capacity

- Certain hydrides, for example borohydrides do not undergo hydrolysis without special catalysis, but the addition of alcohol can change their activity (or reaction route) in such a way, that hydrogen generation may proceed effectively, without the loss of hydrogen capacity
- The use of combined alcoholysis and hydrolysis extends the temperature range of the hydrogen production towards temperatures below freezing  
20 temperature of water.

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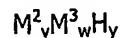
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**CLAIMS**

1. A process for generating hydrogen from a metal hydride comprising:  
reacting a metal hydride with at least one alcohol.
- 5 2. A process according to claim 1, wherein said at least one alcohol is of  
formula ROH in which R is an alkyl group of 1 to 10 carbon atoms.
3. A process according to claim 2, wherein R is an alkyl group of 1 to 6  
carbon atoms.
- 10 4. A process according to claim 2, wherein R is an alkyl group of 1 to 4  
carbon atoms.
5. A process according to claim 1, 2, 3 or 4, wherein said at least one  
alcohol is an aqueous alcohol.
- 15 6. A process according to any one of claims 1 to 4, wherein said at least one  
alcohol comprises a mixture of two or more alcohols.
- 20 7. A process according to any one of claims 1 to 6, wherein said metal  
hydride is a simple metal hydride.
8. A process according to claim 7, wherein said simple hydride is of a metal  
selected from the group consisting of Li, Na, K, Mg, Ca, Zr and Ti.
- 25 9. A process according to any one of claims 1 to 6, wherein said metal  
hydride is a complex metal hydride.
10. A process according to claim 9, wherein said complex hydride is  
30 represented by the formula:



in which

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M<sup>2</sup> is a metal selected from the group consisting of Li, Na, K, Mg, Ca, Fe and Zr;

M<sup>3</sup> is selected from the group consisting of Al, B, Be and Ti;

v is an integer of 1 to 3;

5 w is an integer of 1 to 3; and

y is an integer of 4 to 8.

11. A process according to any one of claims 1 to 10, wherein said metal hydride is contained in a first housing and said at least one alcohol is housed in a  
10 second housing, and wherein said at least one alcohol is fed from said second housing to said first housing and reacts with said metal hydride in said first housing, and recovering generated hydrogen from said first housing.

12. A hydrogen generator comprising:  
15 a) a first housing containing a metal hydride;  
b) a second housing containing at least one alcohol for reaction with said metal hydride;  
c) flow means for delivery of said at least one alcohol from said second housing to said first housing; and  
20 d) hydrogen gas outlet means in said first housing for delivery of generated hydrogen gas from said first housing.

13. A generator according to claim 12, wherein said flow means includes control means for controlled delivery of said at least one alcohol from said  
25 second housing to said first housing.

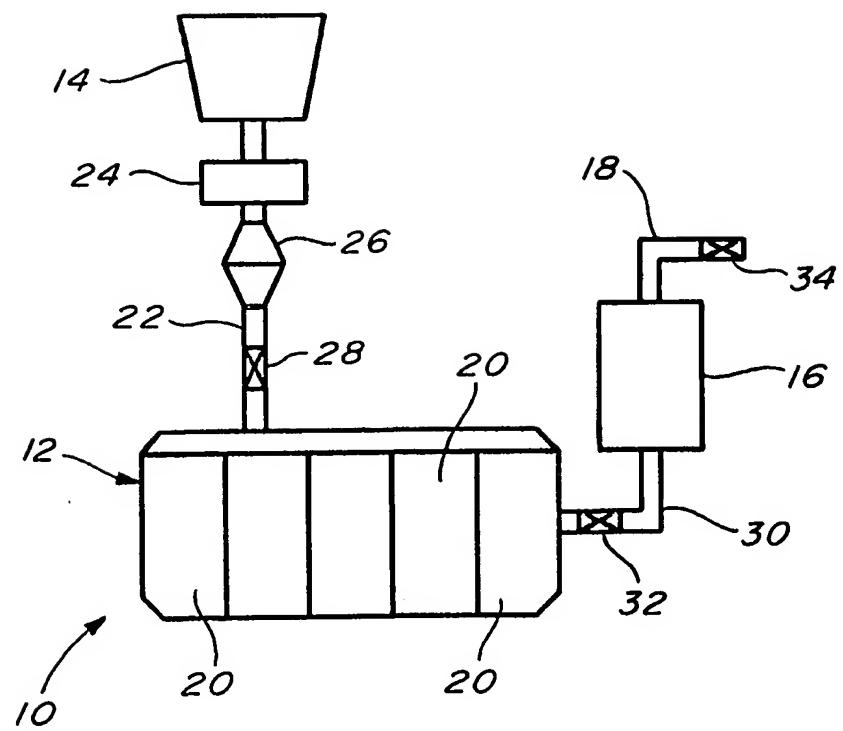
14. A generator according to claim 12 or 13, wherein said hydrogen gas outlet means includes control means for controlling delivery of the generated hydrogen gas from the first housing.  
30

15. A generator according to claim 11, 12, 13 or 14, wherein said at least one alcohol is of formula ROH in which R is an alkyl group of 1 to 10 carbon atoms.

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16. A generator according to claim 15, wherein R is an alkyl group of 1 to 6 carbon atoms.
- 5 17. A generator according to claim 15, wherein R is an alkyl group of 1 to 4 carbon atoms.
18. A generator according to any one of claims 11 to 17, wherein said at least one alcohol is an aqueous alcohol.
- 10 19. A generator according to any one of claims 11 to 18, wherein said at least one alcohol comprises a mixture of two or more alcohols.
- 15 20. A generator according to any one of claims 11 to 19, wherein said metal hydride is a simple metal hydride.
21. A generator according to claim 20, wherein said simple hydride is of a metal selected from the group consisting of Li, K, Na, Mg, Ca, Zr and Ti.
- 20 22. A generator according to any one of claims 11 to 19, wherein said metal hydride is a complex metal hydride.
23. A generator according to claim 22, wherein said complex hydride is represented by the formula:
- 25  $M^2_v M^3_w H_y$   
in which  
 $M^2$  is a metal selected from the group consisting of Li, Na, K, Mg, Ca, Fe and Zr;  
 $M^3$  is selected from the group consisting of Al, B, Be and Ti;  
30  $v$  is an integer of 1 to 3;  
 $w$  is an integer of 1 to 3; and  
 $y$  is an integer of 4 to 8.

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FIGURE 1

## INTERNATIONAL SEARCH REPORT

In	International Application No
PCT/CA 01/00682	

A. CLASSIFICATION OF SUBJECT MATTER			
IPC 7	C01B3/06	B01J7/02	B01J8/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7	C01B	C07F	B01J
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC, COMPENDEX, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	GB 1 189 512 A (CESKOSLOVENSKA AKADEMIE VED) 29 April 1970 (1970-04-29) page 1 -page 2 ----	1-4,8-10
A	US 5 593 640 A (LONG EUGENE ET AL) 14 January 1997 (1997-01-14) claims ----	1,12
A	US 4 155 712 A (TASCHEK WALTER G) 22 May 1979 (1979-05-22) claims -----	1,12

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the International search

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Information on patent family members

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